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权利要求书 1 页 说明书 4 页 附图页数 0 页

[54] 发明名称 白色电致发光材料

[57] 摘要

本发明是一种用于白光显示的电致发光材料,主要由无机荧光材料和蓝色或蓝绿色发光(EL)材料组合而成。利用蓝色或蓝绿色 EL 材料的电致发光与无机荧光材料的光致发光转换按比例混合,形成白色电致发光。蓝色或蓝绿色 EL 材料包含有激活剂和共激活剂。本发明具有亮度高,使用寿命长和发射光谱稳定等优点。可以广泛用于液晶背照明、仪器仪表显示等领域。

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权 利 要 求 书

1、一种白色电致发光材料，其特征是由兰色或兰绿色发光材料与无机荧光材料组合而成，兰色或兰绿色发光材料的电致发光与无机荧光材料的光致发光转换组合成白色电致发光；兰色或兰绿色发光材料中含有激活剂和共激活剂。

2、根据权利要求1所述的白色电致发光材料，其特征是兰色或兰绿色发光材料为 ZnS ，激活剂为 Au 、 Ag 、 Cu 中的一种或一种以上，共激活剂为 Al 、 Mg 、 In 、 Eu 、 Ba 、 Na 、 Br 、 Cl 、 F 、 I 中的一种或一种以上；无机荧光颜料为 $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ ，或者 $(\text{Zn}, \text{Cd})\text{S}:\text{Ag}$ ，或者 $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$ 。

3、根据权利要求2所述的白色电致发光材料，其特征是所用的兰色或兰绿色发光材料发射光谱在 $420\text{nm}\sim 520\text{nm}$ ，无机荧光材料激发光谱在 $400\text{nm}\sim 520\text{nm}$ ，发射光谱在 $520\text{nm}\sim 640\text{nm}$ ，发光峰值在 550nm ；兰色或兰绿色发光材料与无机材料重量比为 $1: 0.1\sim 10$ 。

4、根据权利要求3所述的白色电致发光材料，其特征是兰色或兰绿色发光材料粒度为 $5\sim 35\mu\text{m}$ ，表面包涂在 AlN 、 SiN 、 TiN 、 ZrN 、 Al_2O_3 、 SiO_2 、 TiO_2 、 In_2O_3 保护层；无机荧光材料粒度为 $1\sim 35\mu\text{m}$ 。

5、根据权利要求2所述的白色电致发光材料，其特征是兰色或兰绿色发光材料的激活剂和共激活剂，每种加入量为基质 $1\times 10^{-6}\sim 1\times 10^{-1}$ 克分子/克分子。

6、根据权利要求5或2所述的白色电致发光材料，其特征是在制备发光器件时，需要加入涂粘剂，所用的涂粘剂为环氧树脂，氰乙基纤维素，氰乙基糖，氰乙基醚，二甲基甲酰胺，三乙醇胺，用丝网印刷或喷涂法，涂敷在器件底片上。

说明书

白色电致发光材料

本发明属于发光与显示领域,是一种用于白光显示的电致发光材料。

白色电致发光(EL)技术主要有有机荧光颜料和无机发光材料法。有机荧光颜料法使用粉色有机荧光颜料,将绿色或兰绿色电致发光(EL)材料转换成白色发光。“彩色场效发光显示装置”(CN1150255A, 95120137.9)就是采用有机荧光颜料方法,使用的荧光材料为有机荧光颜料,以有机荧光颜料为主体的白色及其红色等发光。由于有机颜料长期受紫外线照射时,不稳定,为防止发生老化、退色,上述显示装置的荧光彩色印剂有机颜料中加入无机材料 CeO_2 来增强有机材料的稳定性,加入抗紫外吸收剂多种材料防止有机颜料发生老化。无机发光材料法是在兰色或兰绿色发光(EL)材料中按一定比例加入橙色发光(EL)材料,如 $\text{ZnS}:\text{Cu}$ 、 Mn , 组合成白色 EL 发光器件。目前白色发光材料最多的是由 $\text{ZnS}:\text{Cu}$ 与 $\text{ZnS}:\text{Cu}$ 、 Mn 两种发光(EL)材料配比组合成的。如欧司朗-斯维尼亚公司市售产品 700 号、720 号、830 号,均为此类发光形成的白色 EL。在无机发光材料法中,对于有些发光(EL)材料,由于二者老化速度不同,发光颜色会时常发光改变,使白色发光不纯正,应用范围受到极大限制。

用上述两种材料制成的器件,采用场致发光形式,通常为点激发

方式。

本发明利用无机荧光材料，将兰色或兰绿色电致发光材料，在面激发下转换成白色发光的特性，目的是提供一种白色电致发光材料，可用于塑料发光（EL）器件，玻璃发光（EL）器件，搪瓷发光（EL）器件，丝线发光（EL）器件，也适用于液晶背照明，仪表指示，汽车牌照，广告标牌，胸牌，玩具等领域。

本发明的白色发光（EL）材料由兰色或兰绿色发光材料与光致发光材料，即无机荧光材料组合而成。兰色或兰绿色 EL 材料中含有激活剂和共激活剂。兰色或兰绿色发光材料的电致发光与无有机荧光材料的光致发光转换组合成白色电致发光。

本发明使用的兰色或兰绿色 EL 材料为 Zn S，包含的激活剂为 Au、Ag、Cu，共激活剂有 Al、Mg、In、Eu、Dy、Ba、Na、Br、Cl、F、I，至少有一种或一种以上激活剂和共激活剂存在。激活剂与共激活剂，每种加入量在基质中所占比例以克分子计为 $1 \times 10^{-6} \sim 1 \times 10^{-1}$ 克分子/克分子，所述的基质为 ZnS。

本发明涉及的兰色或兰绿色 EL 材料粒度为 $5 \sim 35 \mu m$ ，表面包涂有 AlN、SiN、TiN、ZrN、 Al_2O_3 、 SiO_2 、 TiO_2 、 In_2O_3 保护层。主要发光特征为：当该材料在电场作用下，可发射出光谱为 $420nm \sim 520nm$ 。例如可以使用中国科学院长春物理所的 EL 材料牌号 D417、D447、D417 号兰色 EL 材料，D417 号发光峰值在 $450nm$ ，D447 号发光峰值在 $470nm$ ，D502 号兰白材料发光峰值在 $490nm \sim 500nm$ ，材料粒径 $18 \sim 25 \mu m$ 。

本发明涉及的无机荧光材料可以是稀土氧化物，如 $\text{Y}_3\text{Al}_5\text{O}_{12}$ ：Ce 等，也可以是硫化物，如 $(\text{Zn}、\text{Cd})\text{S}:\text{Ag}, \text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$ 等，上述材料在兰色或兰绿色电致发光激发下能够转换组合成白色、兰色、黄色等多种颜色发光。上述无机荧光材料应具备有如下特性：激发光谱在 $400\text{nm}\sim 520\text{nm}$ ，发射光光谱在 $520\text{nm}\sim 640\text{nm}$ ，发光峰值在 580nm ，材料粒度在 $1\mu\text{m}\sim 35\mu\text{m}$ 。

本发明中的兰色或兰绿色 EL 材料与无机荧光材料重量比（克）为 $1:0.1\sim 10$ 。两者的重量比，即加入量取决于兰色或兰绿 EL 材料发射光谱主峰，光致发光转换材料加入量应依据国际 CIE 标准调配色坐标 X 与 Y 值。

本发明的白色 EL 材料在使用时需要加入涂粘剂，制成各种形式的发光器件。所用的涂粘剂主要成份为：三乙醇胺，环氧树脂，氰乙基纤维素，氰乙基糖，二甲基甲酰胺，氰乙基醚等，混合有涂粘剂的白色 EL 材料可以利用丝网印刷或喷涂法，涂敷在基底上，制成器件。

本发明所述的白色 EL 材料，光致发光材料同 EL 发光材料混合在一起，形成器件的发光层，也可以不进行混合，而把光致发光材料制于 EL 材料的电致发光器件表面，此时的发光层由两层组成，一层为 EL 材料电致发层，另一层为光致发光层。

本发明所用的兰色或兰绿色 EL 材料工作电压在 $40\text{V}\sim 400\text{V}$ ，频率 $50\text{Hz}\sim 1000\text{Hz}$ 。材料合成：在 $300^\circ\text{C}\sim 1300^\circ\text{C}$ ，S 气氛或 H_2S 、HCl 气氛中烧结。

由本发明制备的器件发光强度高，比现有技术提高 $10\%\sim 20\%$ ，

长时间使用不会发生光谱移动，另外成本低，工艺简单。

本发明制备器件的程序为，将发光粉与涂粘剂混合后，印、喷、涂于一电极上，在 120℃ 烘干。再将 BaTi 与涂粘剂混合后，涂于发光层上，印或镀二电极即可。EL 丝线一电极金属铜线，二电极透明导电胶并环绕保护导电细金属丝。涂粘剂各成份可以按下述量配料，环氧树脂 1g，三乙醇胺 0.1g，氰乙基糖 0.1g，氰乙基醚 1g，氰乙基纤维 0.2g，二甲基甲酰胺 1g。上述涂粘剂可与混配好的白色 EL 粉 3g 混均制备器件。

实施例

例 1 选取中国科学院长春物理所 EL 发光材料 D447B 1 克加入 $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ 1 克中，两者充分混合均匀。D447B 材料成份为 $\text{ZnS}:\text{Cu}$ ，共激活剂为 I，激活剂 Cu 与共激活剂 I 的含量分别为基质的 1×10^{-4} 克分子/克分子，发光光谱为 460nm。所制取的白色发光 CIE 标准 $X=0.348, Y=0.351$ 。

例 2 取中国科学院长春物理所 EL 发光材料 D502B100 克，加入 $\text{CaGa}_2\text{S}_4:\text{Ce}$ 70 克中，两者充分混合均匀。D502B 材料成份为 $\text{ZnS}:\text{Cu}$ ，共激活剂为 Br，激活剂 Cu 与共激活剂 Br 的含量分别为基质的 4×10^{-4} 克分子/克分子，发光光谱为 490nm。所制取的白色发光 CIE 标准为 $X=0.312, Y=0.329$ 。



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[54] Title of the Invention: White Electroluminescent Material

[57] Abstract

This invention is an electroluminescent material used in white displays and is comprised primarily of an inorganic fluorescent material and a blue or bluish-green [electro]luminescent (EL) material. The electroluminescence of the blue or bluish-green EL material and the photoluminescence of the inorganic fluorescent material are converted and mixed in proportion to form white electroluminescence. The blue or bluish-green EL material contains an activator and a coactivator. The invention has the advantages of high luminance, long

service life and a stable emission spectrum. It can be widely used in such fields as liquid-crystal back lighting and instrument and meter displays.

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Claims

1. A white electroluminescent material, characterized in that it is comprised of a combination of blue or bluish-green [electro]luminescent material and an inorganic fluorescent material, in that the electroluminescence of the blue or bluish-green [electro]luminescent material and the photoluminescence of the inorganic fluorescent material are converted to form white electroluminescence and in that the blue or bluish-green [electro]luminescent material contains an activator and a coactivator.

2. The white electroluminescent material as described in claim 1, further characterized in that the blue or bluish-green [electro]luminescent material is ZnS, that the activator is one or more of: Au, Ag and Cu, in that the coactivator is one or more of: Al, Mg, In, Eu, Ba, Na, Br, Cl, F and I, and in that the inorganic fluorescent pigment is $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$, $(\text{Zn}, \text{Cd})\text{S}:\text{Ag}$ or $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$.

3. The white electroluminescent material as described in claim 2, further characterized in that the emission spectrum of the blue or bluish-green [electro]luminescent material that is used is 420 nm to 520 nm, that the excitation spectrum of the inorganic fluorescent material is 400 nm to 520 nm, that the emission spectrum is 520 nm to 640 nm, that the luminescence peak value is 550 nm and that the weight ratio of the blue or bluish-green [electro]luminescent material to the inorganic material is 1 : 0.1 to 10.

4. The white electroluminescent material as described in claim 3, further characterized in that the particle size of the blue or bluish-green

[electro]luminescent material is 5 to 35 μm , that the surface is enveloped and coated in an AlN, SiN, TiN, ZrN, Al_2O_3 , SiO_2 , TiO_2^* or In_2O_3 protective layer and that the particle size of the inorganic fluorescent material is 1 to 35 μm .

5. The white electroluminescent material as described in claim 2, further characterized in that the quantity of activator and coactivator of the blue or bluish-green [electro]luminescent material introduced is 1×10^{-6} to 1×10^{-1} mol/mol of substrate.

6. The white electroluminescent material as described in claim 5 or 2, further characterized in that a coating agent must be added when the luminescent component is prepared, the coating agent used being an epoxy resin, cellulose cyanoethylate, cyanoethyl glycoside, cyanoethyl ether, dimethylformamide and triethanolamine and being applied by the screen printing or spray painting method and being spread on the bottom plate of the [luminescent] component.

* This is given as TiO_2 in the Specification—Trans. Note.

Specification

A White Electroluminescent Material

This invention relates to the fields of luminescence and display and is a type of electroluminescent material used in white displays.

The principal white electroluminescence [EL] technologies are the organic fluorescent pigment method and the inorganic photoluminescent materials method. The organic fluorescent pigment method makes use of powdered colored organic fluorescent pigments to convert blue or bluish-green electroluminescent (EL) materials to white luminescence. The “colored-field photoluminescent display apparatus” (CN1150255A, 95120137.9) makes use of the organic fluorescent pigment method. The fluorescent materials used are organic fluorescent pigments, these organic fluorescent pigments having primarily white and red luminescence. When organic pigments are exposed to ultraviolet irradiation for long periods, they become unstable. In order to prevent aging and decoloration, the inorganic material CeO_2 is added to the fluorescent color organic pigment of the aforementioned display apparatus to increase the stability of the organic material and many types of ultraviolet absorption inhibitors are added to prevent aging of the organic pigment. In the inorganic photoluminescent materials method, an orange luminescent (EL) material such as, for example, $\text{ZnS}:\text{Cu}, \text{Mn}$, is added to the blue or bluish-green [electro]luminescent (EL) material in a fixed proportion to form a white EL luminescent component. The most frequently used white luminescent materials

at present are composed of the two [electro]luminescent (EL) materials ZnS:Cu and ZnS:Cu, Mn in compounding ratios. For example, products No. 700, No. 720 and No. 830 marketed by Ousilang-Siweiniya* Company are white EL products formed of this type of luminescence. In the inorganic photoluminescent materials method, the luminescent pigments in several luminescent (EL) materials often undergo changes in luminescence because the two substances are of different aging rates, causing the white luminescence to become impure and greatly limiting their range of use.

The field-induced photoluminescence mode, and, usually, the point excitation mode, is used in making components using these materials.

In this invention, inorganic fluorescent materials are used and blue or bluish-green electroluminescent materials are converted to white luminescent properties under surface excitation. The object is to provide a type of white electroluminescent material that can be used in plastic [electro]luminescent (EL) components, glass [electro]luminescent (EL) components, enamel [electro]luminescent (EL) components and silk filament luminescent (EL) components and that can also be used for liquid-crystal back illumination, instrument displays, automobile license plates, billboards, name tags and toys.

The white [electro]luminescent (EL) material of this invention is comprised of a blue or bluish-green [electro]luminescent material and a photoluminescent material, i.e., an inorganic fluorescent material. The blue or bluish-green EL material contains an activator and a coactivator. The electroluminescence of the

* Phonetic spelling—Trans. Note.

blue or bluish-green [electro]luminescent material and the photoluminescence of the inorganic fluorescent material are converted to white electroluminescence.

The blue or bluish-green EL material of this invention is ZnS. The activators that it contains are Au, Ag and Cu, the coactivators are Al, Mg, In, Eu, Dy, Ba, Na, Br, Cl, F and I, with at least one or more than one activator and coactivator being present. The quantities of activator and coactivator that are introduced account for a ratio of the substrate calculated in moles of 1×10^{-6} to 1×10^{-1} mol/mol. The substrate is ZnS.

The particle diameter of the blue or bluish-green EL material to which this invention relates is 5 to 35 μm and the surface is enclosed and coated in an AlN, SiN, TiN, ZrN, Al_2O_3 , SiO_2 , TiO_2^* or In_2O_3 protective layer. The principal luminescence characteristics are: Under the action of an electric field, said material can emit a spectrum of 420 nm to 520 nm. For example, the EL materials of trademarks D417, D447 and D417 blue EL material of the Changchun Physics Institute of the Chinese Academy of Sciences can be used. The D417 luminescence peak is at 450 nm and the D447 luminescence peak value is at 470 nm. The luminescence peak of D502 white material is at 490 nm to 500 nm and the particle diameter of the material is 18 to 25 μm .

The inorganic fluorescent material to which this invention relates can be a rare earth oxide such as, for example, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and it can also be a sulfide such as, for example, $(\text{Zn}, \text{Cd}) \text{S}:\text{Ag}$, $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$. The aforementioned material can be converted to various types of pigment luminescence such as

* This is given as TiO_2 in claim 4—Trans. Note.

white, blue and yellow under blue or bluish-green electroluminescence excitation.

The aforementioned inorganic fluorescent material should have the following characteristics: An excitation spectrum at 400 nm to 520 nm, an emission spectrum at 520 nm to 640 nm, a luminescence peak at 580 nm and a material particle size of 1 μm to 35 μm .

The weight ratio (g) of the blue or bluish-green EL material and inorganic fluorescent material of this invention is 1 : 0.1 to 10. The weight ratios of the two substances i.e., the quantity added, is determined by the main peak of the emission spectrum of the blue or bluish-green EL material. The quantity of photoluminescent conversion material added should be based on the values of the international CIE standards of color mixing coordinates X and Y.

A coating agent must be added when the white EL material of this invention is used to make various types of photoluminescent components. The principal components of the coating agent used are: triethanolamine, epoxy resin, cellulose cyanoethylate, cyanoethyl glycoside, dimethylformamide and cyanoethyl ether. The white EL material containing the coating agent can be mixed using the screen printing or spray painting method and is spread on the bottom plate of the [luminescent] component to make the component.

The aforementioned photoluminescent material is mixed with the bluish-green EL material to form the luminescent layer of the [luminescent] component. In addition, mixing need not be performed, with the photoluminescent material being placed on the surface of the electroluminescent component. At this time,

the luminiscent layer is composed of two layers. The first layer is the EL material electroluminescent layer and the other layer is the photoluminescent layer.

The working voltage of the blue or bluish-green EL material used in this invention is 40 V to 400 V and the frequency is 50 Hz to 1000 Hz. Synthesis of the material: It is sintered at 300°C to 1300°C and in an S atmosphere or an H₂S, HCl atmosphere.

Components prepared by this invention have a high luminescence intensity that is 10 to 20% higher than that of existing technologies, prolonged use cannot give rise to spectral shift, and, in addition, their cost is low and the technology is simple.

The procedure of preparing components by this invention is to mix the luminescent powder and the coating agent, after which the mixture is [screen] printed, sprayed or applied on an electrode and is dried at 120°C. The first electrode of the EL wire is a copper metal wire and the second electrode is a transparent conductive gel with a surrounding protective, conductive, fine metal filament. Each component of the coating agent can be compounded in the following amounts: epoxy resin, 1 g; triethanolamine, 0.1 g; cyanoglucose, 0.1 g; cyanoether, 1 g; cellulose cyanoethylate, 0.2 g; and dimethylformamide, 1 g. The aforementioned mixture can be mixed with 3 g of well-mixed white EL powder to make the component.

Examples

Example 1. 1 g of EL luminescent material D447B from the Changchun Physics Institute of the Chinese Academy of Science was introduced into 1 g of

$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and the two substances were thoroughly mixed to a homogeneous state. The component of the D447B material was $\text{ZnS}:\text{Cu}$ and the coactivator was I. The content of the activator Cu and the coactivator I was 1×10^{-4} mol/mol of substrate and the luminescence spectrum was 460 nm. The CIE standards of the white luminescence prepared were $X = 0.348$ and $Y = 0.351$.

Example 2. 100 g of EL luminescent material D502B from the Changchun Physics Institute of the Chinese Academy of Science was introduced into 70 g of $\text{CaGa}_2\text{S}_4:\text{Ce}$ and the two substances were thoroughly mixed to a homogeneous state. The component of the D520B material was $\text{ZnS}:\text{Cu}$ and the coactivator was Br. The content of the activator Cu and the coactivator I was 4×10^{-4} mol/mol of substrate and the luminescence spectrum was 490 nm. The CIE standards of the white luminescence prepared were $X = 0.312$ and $Y = 0.329$.